

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

PATENT SPECIFICATION

(11) 1349 118

1349 118

- (21) Application No. 14738/72 (22) Filed 29 March 1972
 (31) Convention Application No. 004530 (32) Filed 29 March 1971
 (31) Convention Application No. 014099 (32) Filed 28 Sept. 1971 in
 (33) Switzerland (CH)
 (44) Complete Specification published 27 March 1974
 (51) International Classification C09B 51/00 C07C 87/60
 (52) Index at acceptance C4P D1N



(54) IMPROVEMENTS IN OR RELATING TO HAIR DYES

(71) We, COSMITAL FRIBOUG S.A., a Swiss Company, of 74 Chemin Ritter, Fribourg, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to hair dyes which contain new aromatic nitro-aminobenzene derivatives nuclear-substituted by chlorine. They serve especially for cosmetic purposes.

It is known that for dyeing human hair one uses nitro-aminobenzene compounds such as 1,4 - diamino - 2 - nitrobenzene or its N - substituted derivatives. These dyes are used especially when hair colouration in red colour tones are necessary. However, it has appeared that certain disadvantages pertain to the dyestuffs, so that satisfactory dyeing results with hair dyes containing such red components are not yet ensured. This applies especially to the inadequate stability of the colour tones obtained. Thus colour tone shifts frequently occur which are caused by skin secretions such as the acid perspiration and the action of sunlight upon the dyed hair. Even in the cases where an acid after-rinse is expedient after the dyeing treatment, the inadequate stability of the colouration obtained makes itself noticeable in a disadvantageous manner.

Now it has been found that these disadvantages can be largely avoided if the hair dye compositions according to the present application are used. The hair dye compositions according to the invention are characterised in that they contain dyestuffs of the general formula:



40 in which R₁ and R₂, similarly or dissimilarly,

[Price 25p]

are to signify a hydrogen atom or a hydroxy-ethyl group ($-\text{C}_2\text{H}_4\text{OH}$).

These dyestuffs are new and produce hair colourations in pure red to purple colour tones, of outstanding stability.

Their production, which is described in greater detail takes place in analogy with the procedures known *per se*, namely in one case from chloro - p - phenylene - diamine - sulphate by acetylation, nitration and saponification, or subsequent ethoxylation. In the other case commencement is made from 1,5 - dichloro - 4 - aminobenzene, whereupon nitration, acetylation, reaction with ethanolamine and subsequent saponification or further ethoxylation takes place.

The hair dye compositions according to the invention with a content of dyestuffs of the above formula concern both those which are to be applied without addition of an oxidising agent and those with which the addition of an oxidising agent is necessary.

These hair dyes, without addition of oxidising agent are those which can also contain other dyestuffs which directly are coloured when applied and therefore colour the hair, as well as the dyestuffs of the stated formula. Of these dyestuffs known for hair dyeing, by way of example the following classes should be mentioned.

Aromatic nitro dyestuffs (for example 1,2 - diamino - 4 - nitrobenzene), azo dyestuffs (for example Azilanbraun R), anthraquinone dyes (for example "Cellitone" of the firm BASF), triphenylmethane dyes (for example methylviolet B), and the dyestuffs of these classes can have acid, non-ionic or basic character according to the nature of their substituents.

With the hair dye compositions of the invention, which comprise mixtures of dyestuffs as above, apart from pure fashion tones it is also possible to achieve fashionable blonde and brown tones of outstanding stability.

The form of preparation of these hair dyes is preferably that of a liquid solution, and water or mixtures of water with low molecular weight alcohols, such especially as ethanol

or isopropanol, come under consideration as solvents.

The dyestuffs of the stated formula should be contained in these liquid dye compositions in a concentration of 0.01—1.0% by weight, preferably 0.05—0.5% by weight. The total dyestuff content lies in the limits of 0.01—3.0% by weight.

The pH value of these dye compositions lies in the range of 7—10.5, especially at pH 7.5—9.5, the adjustment of the desired pH value taking place mainly with ammonia, but it can also be effected with organic amines for example monoethanolamine or triethanolamine.

Their use takes place in the usual way by application of the composition to the hair, with which it remains in contact for a period between 5 and 30 minutes. Then the hair is rinsed with water, possibly also with a weak organic acid, and dried. As weak organic acids there may be used for example citric acid or tartaric acid.

The above-described hair dye composition without addition of oxidising agents can of course also contain cosmetic polymerisates, whereby setting of the hair is achieved simultaneously with the dyeing.

Of the polymerisates known for this purpose in cosmetics mention should be made by way of example of polyvinylpyrrolidone, polyvinylacetate, polyvinylalcohol or polyacrylic compounds such as acrylic acid or methacrylic acid polymerisates, basic polymerisates of esters of these two acids and amino alcohols, or salts or quaternisation products thereof, polyacrylonitrile, polyvinyl lactams and copolymerisates of such compounds as polyvinylpyrrolidonevinyl acetate.

The polymerisates are contained in these compositions in quantities of about 1—4% by weight. The pH values of compositions containing polymerisates lie in the region of 6.0—9.0.

The use of these hair dyes with additional setting takes place in the known manner by setting (securing) of the hair while dressing and subsequent drying.

Of course the above-described hair dye compositions without addition of oxidising agent may possibly contain further cosmetic additives, for example care media, wetting agents, thickeners, softeners and perfume oils.

To the object of the present invention also pertains, as initially mentioned, those hair dye compositions to which the addition of an oxidising agent is necessary. Apart from the dyestuffs according to the stated formula they may also additionally contain known oxidising dyestuffs which require an oxidative development.

These oxidation dyestuffs are mainly aromatic p-diamines and p-aminophenols for example p - toluyldiamine, p - phenylene-

diamine or p - aminophenol compounds, which are combined with so-called modifiers, for example m - phenylenediamine, resorcin, m - aminophenol and others, for the purpose of shading the colourations.

Such oxidation dyestuffs, which are known and usual for hair dyeing are described *inter alia* in the book by E. Sagarin "Cosmetics", Science and Technology (1957), Interscience Publishers Inc., New York, pages 503 et seq.

As well as pure fashion tones it is also possible to obtain fashionable blonde and brown tones with mixtures of these oxidation dyestuffs and the dyestuffs according to the stated formula.

The dyestuffs according to the formula are contained in the dye compositions with addition of oxidising agent in a concentration of 0.01—1.0% by weight, preferably 0.05—0.5% by weight. The total dyestuff content in these dyes amounts to 0.1—5.0% by weight.

The dye compositions are adjusted to alkalinity, preferably to pH values of 9.5—10.5, the adjustment taking place especially with ammonia. However for this purpose it is also possible to use organic amines, for example monoethanolamine or triethanolamine. Hydrogen peroxide or its addition compounds come mainly under consideration as oxidising agents for the development of the hair colourations. These hair dyes are preferably in the form of a cream or a gel.

Their application takes place in known manner, in that before the treatment the hair dyes are mixed with the oxidising agent and the mixture is applied to the hair.

After a period of about 10—45 minutes, the hair is rinsed with water, possibly subsequently with a weak organic acid for example citric acid or tartaric acid, and dried.

These hair dyes with addition of oxidising agent can of course contain known and usual cosmetic additions for example anti-oxidants, complex formers, thickeners, tensides, care media and perfume oils.

The following examples illustrate the invention:

Example 1

The liquid hair dye of composition: 115

0.5 g hydroxyethylcellulose (Tylose Registered Trade Mark)

5.0 g lauryl alcohol - diglycoether sulphate (28% aqueous solution)

15.0 g isopropylalcohol 120

0.1 g 1,4 - diamino - 2 - nitro - 5 - chlorobenzene

0.03 g ammonia (25%)

79.37 g water

100.00 g

is applied to white human hair and permitted

to act for ten minutes. After rinsing with water and drying, the hair is dyed bright red.

Example 2

5	2.00 g	polyvinylpyrrolidone
	0.10 g	glycerine
	40.00 g	isopropylalcohol
	0.15 g	1,4 - diamino - 2 - nitro - 5 - chlorobenzene
	57.75 g	water
10	100.00 g	

White human hairs are dressed with the setting dye solution and dried. The hair is coloured bright red and strengthened.

Example 3

15	35.0 g	oleic acid
	15.0 g	isopropyl alcohol
	18.0 g	ammonia (25%)
	0.2 g	bisodium ethylenediamine - tetra - acetate
20	0.1 g	sodium sulphite
	0.8 g	p - toluylenediamine - sulphate
	0.2 g	resorcin
	0.05 g	m.aminophenol
25	0.2 g	1 - amino - 2 - nitro - 4 - β - hydroxyethylamino - 5 - chlorobenzene
	30.45 g	Water
	100.00 g	

- 50 ml of the above hair dye are mixed shortly before use with 50 ml hydrogen peroxide solution (6%). The gel obtained is then applied to grey human hair and permitted to act for 30 minutes. The hair is then rinsed with water and dried. The hair has received a reddish-blond colouration.

Example 4

	2.0 g	copolymerisate of vinylpyrrolidone-vinyl acetate 60:40
	0.1 g	glycerine
40	40.0 g	isopropyl alcohol
	0.15 g	1 - amino - 2 - nitro - 4 - β - hydroxyethylamino - 5 - chlorobenzene
	57.75 g	water
45	100.00 g	

White human hair is dressed with this setting dye solution and then dried. The hair is dyed bluish-red and strengthened.

Example 5

A	liquid hair dye consisting of	50
5.0 g	laurylalcohol - diglycolether sulphate (28% aqueous solution)	
0.5 g	hydroxyethylcellulose (tylose)	
15.0 g	ethylalcohol	
0.1 g	1 - amino - 2 - nitro - 4 - β - hydroxyethylamino - 5 - chlorobenzene	55
0.03 g	ammonia (25%)	
79.37 g	water	
100.00 g		60

is applied to white human hair and left to act for 10 minutes. Then the hair is rinsed with water and dried. The hair has received a bluish red colouration.

Example 6

The liquid hair dye of composition		65
0.5 g	hydroxyethylcellulose (tylose)	
5.0 g	laurylalcohol - diglycolether sulphate (28% aqueous solution)	
15.0 g	isopropylalcohol	70
0.1 g	1 - 4 - diamino - 2 - nitro - 5 - chlorobenzene	
0.3 g	Acilanbraun R (C.I. 14,805)	
0.03 g	ammonia (25%)	
79.07 g	water	75
100.00 g		

is applied to white human hair and permitted to act for 10 minutes. After rinsing with water and drying the hair is dyed red-brown.

Example 7

The liquid hair dye of composition		80
0.5 g	hydroxyethylcellulose (tylose)	
5.0 g	laurylalcohol - diglycolether sulphate (28% aqueous solution)	
15.0 g	isopropylalcohol	85
0.1 g	1 - β - hydroxyethylamino - 2 - nitro - 4 - amino - 5 - chlorobenzene	
0.03 g	ammonia (25%)	
79.37 g	water	90
100.00 g		

is applied to white human hair and permitted to act for 10 minutes. After rinsing with water and drying the hair is dyed a purple colour.

Example 8

	2.00 g	polyvinylpyrrolidone
	0.10 g	glycerine
	40.00 g	isopropylalcohol
5	0.15 g	1 - β - hydroxyethylamino - 2 - nitro - 4 - amino - 5 - chlorobenzene
	57.75 g	water
	100.00 g	

10 White human hair is dressed with the setting dye solution and dried. The hair is dyed a purple colour and strengthened.

Example 9

	35.0 g	oleic acid
15	15.0 g	isopropylalcohol
	18.0 g	ammonia (25%)
	0.2 g	bisodium ethylenediamine - tetraacetate
	0.1 g	sodium sulphite
20	0.8 g	p - toluylenediamine - sulphate
	0.2 g	resorcin
	0.05 g	m - aminophenol
	0.2 g	1,4 - di - (β - hydroxyethylamino) - 2 - nitro - 5 - chlorobenzene
25	30.45 g	water
	100.00 g	

50 ml of the above hair dye are mixed shortly before use with 50 ml of hydrogen peroxide solution (6%). The gel obtained is then applied to grey human hair and permitted to act for 30 minutes. Then the hair is rinsed with water and dried. The hair has received a reddish-blonde colouration.

Example 10

35	2.0 g	copolymerisate of vinylpyrrolidone-vinylacetate 60:40
	0.1 g	glycerine
	40.0 g	isopropylalcohol
40	0.15 g	1,4 - di - (β - hydroxyethylamino) - 2 - nitro - 5 - chlorobenzene
	57.75 g	water
	100.00 g	

White human hair is dressed with this setting dye solution and then dried. The hair is dyed violet-red and strengthened.

Example 11

A liquid hair dye, consisting of

	5.0 g	lauryl alcohol - diglycoethersulphate (28% aqueous solution)
50	0.5 g	hydroxyethylcellulose (tylose)
	15.0 g	ethyl alcohol
	0.1 g	1,4 - di - (β - hydroxyethylamino) - 2 - nitro - 5 - chlorobenzene
	0.03 g	ammonia (25%)
55	79.37 g	water
	100.00 g	

is applied to white human hair and permitted to act for 10 minutes. Then the hair is rinsed with water and dried. The hair has received a violet-red colouration.

60

Example 12

The liquid hair dye of composition

	0.5 g	hydroxyethylcellulose (tylose)
	5.0 g	lauryl alcohol - diglycoethersulphate (28% aqueous solution)
65	15.0 g	isopropylalcohol
	0.1 g	1 - β - hydroxyethylamino - 2 - nitro - 4 - amino - 5 - chlorobenzene
	0.3 g	Acilanbrain R (C.I. 14,805)
	0.03 g	ammonia (25%)
	79.07 g	water
	100.00 g	

is applied to white human hair and permitted to act for 10 minutes. After rinsing with water and drying the hair is dyed red-brown.

75

Production process

A) Production of 1,4 - diamino - 2 - nitro - 5 - chlorobenzene

a) 1000 g of chloro - p - phenylenediamine-sulphate are dissolved in water and the base is freed with ammonia. The precipitated base is drawn off by suction and dried. Yield: 600 g (chloro - p - phenylenediamine). 600 g of base are heated with 500 ml. of acetic acid and 1 kg of acetic acid anhydride for one hour to 140°C. It is poured on to ice and the acetyl compound precipitates out. It is drawn off by suction and dried. Yield: 645.5 g chloro - 1,4 - diacetamidobenzene, m.p.: 202—203°C.

80

85

90

b) 224.5 g (1 mol) of chloro - 1,4 - diacetamidobenzene are dissolved in 1,000 ml of conc. sulphuric acid at -15°C. Then nitration is effected at -5°C with a mixture of 400 ml of sulphuric acid (1.84) and 40 ml HNO₃ (d=1.5). Then stirring is effected for 1 hour and the solution is poured on to ice. The precipitated acetyl compound is drawn off by suction and well washed with water. The still moist acetyl compound is saponified with 1 litre of hydrochloric acid (half concentrated). It is cooled and mixed with ammonia. Yield: 137 g of 1,4 - diamino - 2 - nitro - 5 - chlorobenzene m.p. 157°C.

100

105

Analysis: C₉H₈ClO₂N₂

	C	H	N
calc.:	38.42	3.23	22.40
found:	38.54	3.21	22.32
	38.32	3.24	22.46

110

B) Production of 1 - amino - 2 - nitro - 4 - β - hydroxyethylamino - 5 - chlorobenzene

18.7 g (0.1 mol) of 1,4 - diamino - 2 -

nitro - 5 - chlorobenzene are dissolved in 20 ml of methylglycol and 12 g of ethylene - chlorohydrin (1.5 mol), and brought to 120°C (bath temperature). Now 6.6 g of sodium hydroxide in 60 ml of water are dripped in very slowly over 3 hours. Heating is effected for a further hour and then testing is effected by chromatography as to whether the starting compound has reacted. After cooling the solution is diluted with water and the precipitated hydroxyethylated compound is drawn off by suction. The product is recrystallised from water and then 20% acetic acid. Yield 4.5 g, m.p.: 130—131°C.

15 Analysis: $C_8H_{10}ClO_2N_2$

	C	H	N
calc.:	41.48	4.35	18.14
found:	41.74	4.37	18.23
	41.36	4.31	18.23

20 C) Production of 1 - β - hydroxyethylamino - 2 - nitro - 4 - amino - 5 - chlorobenzene

a) 648 g (4 mol) of 1,5 - dichloro - 4 - aminobenzene are dissolved in 3,200 ml of conc. H_2SO_4 at -10°C. Nitration is now effected with a mixture of 1600 ml conc. H_2SO_4 and 160 ml. HNO_3 (d=1.5) at approx. 0°C. After complete addition, reaction is permitted for 1 hour. The reaction mixture is then tipped on to 16 l. of ice water. The precipitated nitro compound is drawn off by suction and recrystallised from isopropanol/water. Yield: 455 g 2 - nitro - 4 - amino - 1,5 - di - chlorobenzene, m.p.: 103—104°C.

35 b) 455 g (2.2 mol) of 2 - nitro - 4 - amino - 1,5 - dichlorobenzene are dissolved in 1 litre of CH_3COOH and acetylated under heat with 300 ml of acetic acid anhydride. After cooling the solution is poured on to 10 litres of ice water. The precipitated acetyl compound is drawn off by suction, washed and dried. Yield: 500 g 2 - nitro - 4 - acetylamino - 1,5 - dichlorobenzene m.p.: 128—130°C.

45 c) 500 g (2 mol) of 2 - nitro - 4 - acetyl-amino - 1,5 - dichlorobenzene are dissolved in 1,900 ml of methylglycol. 246 g of ethanolamine are added by drops at 140°C bath temperature. Then heating is effected for a further 1 hour with agitation. After cooling the solution is poured on to 12 litres of water. The precipitated product is drawn off by suction and washed with water. m.p.: 183—185°C.

55 The still damp acetyl compound is saponified with 2,000 ml of alcoholic hydrochloric acid (1:1). The hydrochloride formed is drawn off by suction and washed with a little cold alcohol.

60 Now the compound is dissolved in water and the base is obtained by the addition of ammonia. After drawing off by suction and drying, recrystallisation is effected from acetic acid ethylester. Yield: 113 g 1 - β - hydroxy-

ethylamino - 2 - nitro - 4' - amino - 5 - chlorobenzene, m.p.: 149°C.

65

Analysis: $C_8H_{10}N_2O_2Cl$

	C	H	N
calc.:	41.48	4.35	18.44
found:	41.51	4.50	18.60

D) Production of 1,4 - Di - (β - hydroxyethylamino) - 2 - nitro - 5 - chlorobenzene

70

75.0 g (0.33 mol) 1 - β - hydroxyethylamino - 2 - nitro - 4 - amino - 5 - chlorobenzene are dissolved in 150 ml of methylglycol and 36 g (0.5 mol) of ethylenechlorohydrin. With a bath temperature of 130°C., 19.8 g of NaOH in 180 ml of water are permitted to drip in, with agitation, in the course of 3 hours. After cooling the end product is drawn off by suction and recrystallised out of water. Yield: 35 g of 1,4 - di - (β - hydroxyethylamino) - 2 - nitro - 5 - chlorobenzene, m.p. 127—128°C.

75

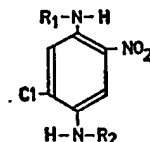
Analysis: $C_{10}H_{14}N_2O_4Cl$

85

	C	H	N
calc.:	43.56	5.13	15.24
found:	43.31	5.20	15.40

WHAT WE CLAIM IS:—

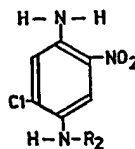
1. Hair dyeing compositions comprising a dyestuff of the general formula



in which R_1 and R_2 similarly or dissimilarly, signify a hydrogen atom or a hydroxyethyl group, and hair-cosmetic additives known per se.

95

2. Hair dyeing compositions according to Claim 1 comprising a dyestuff of the general formula



100

in which R_2 signifies a hydrogen atom or a hydroxyethyl group.

3. Hair dyeing compositions according to either of Claims 1 and 2, characterised in that they additionally contain hair dyestuffs of the nitro, azo, anthraquinone or triphenylmethane series.

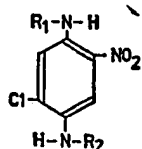
105

4. Hair dyeing compositions according to any of Claims 1 to 3, characterised in that they additionally contain cosmetic polymerisates for the simultaneous setting of the hair.

5. Hair dyeing compositions according to any of Claims 1 and 2, characterised in that they additionally contain oxidation dyestuffs, and shading dyestuffs.

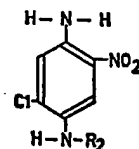
- 10 6. Hair dyeing compositions according to Claims 1 to 5, characterised in that they additionally contain as cosmetic additives one or more of care media, tensides, thickeners, perfume oils, softeners, anti-oxidants and complex formers.

- 15 7. Dyestuffs of the general formula



- 20 in which R_1 and R_2 , similarly or dissimilarly, signify a hydrogen atom or a hydroxy ethyl group.

8. Dyestuffs according to Claim 7, characterised by the general formula



in which R_2 signifies a hydrogen atom or a hydroxyethyl group.

9. 1,4 - diamino - 2 - nitro - 5 - chlorobenzene.

10. 1 - amino - 2 - nitro - 4 - β - hydroxyethylamino - 5 - chlorobenzene.

11. 1 - β - hydroxyethylamino - 2 - nitro - 4 - amino - 5 - chlorobenzene.

12. 1,4 - di - (β - hydroxyethylamino) - 2 - nitro - 5 - chlorobenzene.

WITHERS & ROGERS,
Chartered Patent Agents,
148—150 Holborn,
London, EC1N 2NT
Agents for the Applicants.